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DETERMINATION OF FATTY ACID COMPOSITIONAL FINGERPRINTS OF DIFFERENT VEGETABLE OILS AND THEIR EFFECTIVENESS FOR ADULTERATION DETECTION IN COMMERCIAL OILS

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ABSTRACT

Authenticity of vegetable oils is of concern for commercial and health reasons. Fatty acid composition in the seed oil of locally grown crops like corn, canola, soybean, sunflower and cotton were determined by GC/FID. From these fatty acids compositional fingerprints certain factors were derived to be used as purity criteria for specific vegetable oil. The derived factors were applied for the detection of adulteration in market samples of different edible oils (corn, canola, soybean and sunflower). The results revealed that corn, canola and soybean oil of different brands were pure, but all the sunflower oil samples were found adulterated at varying levels (low to high). One brand, labeled sunflower oil, contained 100% canola oil.

Keywords: Vegetable oils; Fatty acids; Gas chromatography; Commercial oils; Adulteration detection.

INTRODUCTION

Oils and fats are very important food component. Since the turn of the century, vegetable oils have supplanted lard and beef tallow as the major source of dietary fat. Nutritional effects of edible oils with respect to absorption, growth, food efficiency and biosafety are considered to be significant in modern living. On the basis of the expending market for vegetable oils, their authenticity has become an important subject from both commercial and health perspective. Authenticity (Lee, 1999) covers many aspects, including adulteration, mislabeling, characterization and misleading origin. Blending cheaper oil with premium oil has always been profitable business for unscrupulous traders. Higher the price of premium oil, greater is the propensity to adulterate it with low priced oil. Various countries have reported the adulteration of high priced oil. Reports from India indicate that high-priced refined sunflower oil is being mixed with cheaper oils (Chandrashekhar, 2003).

Oil quality depends on its fatty acid composition (saturated, monounsaturated and polyunsaturated fatty acids). For the detection of adulteration of edible oils, the use of chromatographic techniques is an effective way (Aparicio and Aparicio-Ruz, 2000). Coupled techniques have also been used to detect adulteration. Kelly *et al*. (1997) used gas chromatography-combustion-stable isotope ratio mass spectrometry (GC-CSIR-MS) to investigate the authenticity of groundnut, palm, rapeseed and sunflower oils. In Pakistan the most commonly used cooking oils are Corn, Sunflower, Canola and Soybean. Corn and Sunflower oils are expensive than Canola, Soybean and cotton seed oils in the international market. Keeping in view the circumstances, efforts were made to utilize gas chromatography to determine fatty acid profile of the pure seed oils extracted from locally grown corn, canola, sunflower, cotton seed and soybean crops and such factors were derived which could be applied for authentication of commercial oils being sold in the market for edible purpose.

MATERIALS AND METHODS

Collection of samples

Samples of Corn oil (MS-1), sunflower oil (MS-2, MS-3 and MS-4), Canola oil (MS-5, MS-6 and MS-7) and Soybean oil (MS-8, MS-9 and MS-10) were purchased from the market in one Kg packing. The seeds of corn varieties (Composit-20, Corn-DC and Maize Mixture), sunflower varieties (FH-86, FH-131, FH-136, and FH-141), canola varieties (OSCAR, Shiralee and CON-II) and soybean variety (Faisal) were collected from Ayub Agricultural Research Institute (AARI), Faisalabad, Pakistan. The seeds of cotton varieties (NIAB-999, NIAB-98, NIAB-111, NIBGE-1 and CIM-448) were collected from Mutation Breeding Div. NIAB, Faisalabad, Pakistan. Soxhlet apparatus was used for the extraction of oil from the seeds using petroleum ether as solvent.

Fatty acid composition of the oils

After esterification (Shibahara *e. al*., 1996) quantitative analysis of the fatty acid methyl esters of each oil was carried out by Gas chromatograph PERKIN ELMER-3920 attached with Flame Ionization Detector on 2m x 2mm, i.d. glass column packed with 20% DEGS. Gas chromatographic conditions were: injector temperature, 250^{o}C;

detector temperature, 275 ^{o}C and column temperature, isothermal at 200 ^{o}C. Flow rate of nitrogen, 30 mL min^{-1}; hydrogen pressure 20 psi; air pressure, 50 psi. Fatty acid methyl esters kit of Poly Science Corporation 6366 Gross Point Road, Niles, IL 60648 was used as standard.

Table 1. Fatty acid profile determined by GLC in the oils extracted from the seeds of different crops.

Oil seed crops/ varieties		Fatty acids (%)						
		16:0	**18:0**	**18:1**	**18:2**	**18:3**	**20:1**	**22:1**
Maize	Composit-20	15.74 ±0.16	2.07 ± 0.08	29.80 ±1.06	51.20 ±0.86	1.16 ±0.09	-	-
	Corn-DC	16.26 ±0.68	1.88 ±0.12	30.25 ±1.08	50.23 ±0.68	1.35 ±0.14	-	-
	Maize mixture	16.94 ±0.14	2.49 ±0.14	30.54 ±1.34	48.79 ±1.48	1.22 ±0.14	-	-
Sunflower	FH-86	7.17 ±0.64	3.51 ±0.22	51.70 ±1.08	37.45 ±0.49	0.55 ±0.17	-	-
	FH-131	6.89 ±0.34	2.51 ±0.16	42.69 ±1.06	47.69 ±1.12	-	-	-
	FH-136	6.08 ±0.68	2.69 ±0.20	50.07 ±0.82	41.18 ±0.50	-	-	-
	FH-141	7.07 ±0.38	2.44 ±0.38	43.45 ±0.65	47.05 ±0.83	-	-	-
Canola	OSCAR	5.95 ±0.78	2.05 ±0.22	61.57 ±2.32	19.21 ±0.92	8.07 ±0.74	1.89 ±0.44	1.27 ±0.20
	Shiralee	6.20 ±0.49	2.14 ±0.32	62.67 ±2.83	17.20 ±1.21	9.10 ±0.78	1.23 ±0.25	1.50 ±0.26
	CON-II	6.41 ±0.56	1.88 ±0.32	59.11 ±1.02	22.71 ±2.08	7.60 ±0.96	1.45 ±0.34	0.85 ±0.30
Cotton	NIAB-999	28.54 ±1.34	1.70 ±0.20	19.15 ±1.24	50.65 ±1.96	-	-	-
	NIAB-98	27.58 ±0.92	1.65 ±0.26	15.46 ±1.42	55.31 ±1.96	-	-	-
	NIAB-111	30.16 ±1.16	1.52 ±0.25	20.42 ±1.12	47.79 ±1.95	-	-	-
	NIBGE-1	27.00 ±1.30	1.86 ±0.26	17.61 ±0.72	53.53 ±1.02	-	-	-
	CIM-448	28.03 ±2.29	2.03 ±0.40	24.33 ±2.03	45.60 ±0.87	-	-	-
Soybean	Faisal	14.15 ±0.80	4.23 ±0.26	23.25 ±1.05	51.00 ±0.82	7.37 ±0.55	-	-

Values (mean ± SD) are average of duplicate samples analyzed in triplicate

RESULTS AND DISCUSSION

Fatty acid composition in the seed oil of different varieties of corn, sunflower, canola, cotton and soybean grown in our local environment was determined by GLC (Table 1). The identified fatty acids were palmatic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), linolenic (18:3), ecosenoic (20:1) and erucic (22:1). In different oils it was observed that there was a clear and wide variation in the composition of some fatty acids like; palmatic, oleic, oleic+linoleic and linolenic. Whereas, ecosenoic and erucic acid were found only in canola oil. The distinctive fatty acids (Table 2) in different oils were derived from the fatty acid profile results of all the oils under study. The percentage of distinctive fatty acids (Table 2) indicates three different levels of palmatic acid (16:0); low (5-7%), intermediate (13-16%) and high (27-30%). Low palmatic acid composition (5-7%) is common for sunflower and canola oils. Therefore, to distinguish canola oil from sunflower oil, oleic acid (18:1) will have to be considered. If it is significantly high i.e. 58-63% and erucic acid (22:1) is less than 2% it could be pure canola oil. Kfapoulas and Emmanouilidou, (1981) reported that palmatic acid could be used as an indicator of adulteration of cotton seed oil

by palm olein, since cotton seed oil has a palmatic acid content of between 21 and 26% wereas palm olein contains around 40% palmatic acid. They also indicated that linolenic acid content is good indicator of purity if sunflower oil is suspected of being adulterated with cheaper soybean or rapeseed oils. Sun flower oil contains less than 0.1% of this acid vs. 10% in rapeseed and soybean oils. In our findings (Table 1 & 2) the other distinguishing factor for sunflower oil is also linolenic acid (18:3), which is almost negligible (0-0.6%) in sunflower oil as compared to canola oil (7-10%). Meydani *et al*., (1991) reported 0.1% linolenic acid in sunflower oil, however, most of the researchers have reported it to be nil. Further sunflower oil has highest level of 18:1+18:2 (89-92%). Our findings are close to Unger and Thompson (1982), they reported about 90% unsaturated and 10-15% saturated fatty acids in sunflower oil. Intermediate palmatic acid (16:0) level (13-16%) is common for corn and soybean oils. Therefore, to differentiate these two oils, the composition of linolenic acid (18:3) will have to be considered. If it is 1-2% it could be pure corn oil, but if it is significantly high i.e. 6-8% then it could be pure soybean oil. Similarly in case of cottonseed oil, the distinguishing factor is highest level of palmatic acid (16:0), that is, 27-30% and absence of linolenic acid. Therefore, our finally derived purity parameters (ranges of distinguishing fatty acids for different oils) are shown in Table 3. The fatty acid compositions determined in the oils of these oil seed crops were quite close to the fatty acid compositions reported in literature.

Table 2. Percentage of distinctive fatty acids in different vegetable oils.

Oil seed crops/ varieties		**Fatty acids (%)**				
		Palmatic acid (16:0)	**Oleic acid (18:1)**	**Linolenic acid (18:3)**	**Oleic + Linoleic acid (18:1+18:2)**	**Erucic acid (22:1)**
Maize	Composit-20	15.74	29.80	1.16	81.0	-
	Corn-DC	16.26	30.25	1.35	80.48	-
	Maize mixture	16.94	30.54	1.22	79.33	-
Sunflower	FH-86	7.17	51.70	0.55	89.15	-
	FH-131	6.89	42.69	-	90.38	-
	FH-136	6.08	50.07	-	91.25	-
	FH-141	7.07	43.45	-	90.05	-
Canola	OSCAR	5.95	61.57	8.07	80.78	1.27
	Shiralee	6.20	62.67	9.10	79.87	1.50
	CON-II	6.41	59.11	7.60	81.82	0.85
Cotton	NIAB-999	28.54	19.15	-	69.80	-
	NIAB-98	27.58	15.46	-	70.77	-
	NIAB-111	30.16	20.42	-	68.21	-
	NIBGE-1	27.00	17.61	-	71.14	-
	CIM-448	28.03	24.33	-	69.93	-
Soybean	Faisal	14.15	23.25	7.37	74.25	-

Table 3. Selected purity parameters (ranges of distinguishing fatty acids for different oils).

Oil	16:0 (%)	18:1(%)	18:3 (%)	18:1+18:2 (%)	22:1 (%)
Corn	13 - 16	-	1 - 2	-	-
Sunflower	5 - 7	-	0 - 0.6	89 – 92	-
Canola	5 - 7	58 - 63	7 -10	-	0 - 2
Cotton seed	27 - 30	-	-	-	-
Soybean	13 - 16	-	6 - 8	-	-

Table 4. Fatty acids composition of market samples of different vegetable oils of different vendors, determined by GLC.

Oil name	Vendor	Fatty acids (%age)						
		16:0	18:0	18:1	18:2	18:3	20:1	22:1
Corn	MS-1	14.99 ±0.66	2.32 ±0.20	28.33 ±1.53	52.5 ±1.99	1.77 ±0.28	-	-
Sunflower	MS-2	10.13 ±1.15	3.26 ±0.56	42.71 ±1.75	34.91 ±1.18	8.29 ±0.57	-	-
	MS-3	7.97 ±0.80	3.43 ±0.48	49.57 ±1.28	36.91 ±0.20	1.82 ±0.24	-	-
	MS-4	5.75 ±0.82	1.74 ±0.44	62.32 ±2.47	19.76 ±0.98	8.64 ±0.68	1.77 ±0.40	-
Canola	MS-5	5.71 ±0.48	2.09 ±0.16	57.38 ±1.54	24.45 ±0.42	8.12 ±0.60	1.49 ±0.22	0.46 ±0.04
	MS-6	6.39 ±0.76	1.90 ±0.22	59.19 ±1.24	22.29 ±0.25	8.77 ±0.66	1.34 ±0.16	-
	MS-7	5.03 ±0.04	1.90 ±0.13	58.98 ±1.24	20.28 ±0.88	11.55 ±0.68	1.46 ±0.25	-
Soybean	MS-8	12.75 ±0.52	4.25 ±0.62	25.62 ±1.43	49.02 ±1.28	8.30 ±0.61	-	-
	MS-9	13.27 ±0.86	4.09 ±0.42	20.61 ±0.84	52.46 ±1.12	9.53 ±1.28	-	-
	MS-10	13.63 ±0.88	4.32 ±0.54	22.29 ±1.06	51.20 ±1.64	8.55 ±0.78	-	-

Values (mean ± SD) are average of duplicate samples analyzed in triplicate.

Table 4 shows the fatty acid composition of market samples of corn, sunflower, canola and soybean oils of different vendors. Fatty acid composition of corn oil sample (MS-1) showed palmatic acid 14.99% and linolenic acid 1.77%. Both these compositions lie between the limits as described in Table 3 for purity criteria of corn oil. Therefore, the corn oil sample MS-1 was found pure. In case of sunflower oil samples MS-2 indicated the presence of palmatic acid (10.13%), linolenic acid (8.29%) and 18:1+18:2 (77.62%) which significantly differs from the purity parameters for sunflower oil defined in Table 3 i.e. palmatic acid (5-7%), linolenic acid < 0.6% and 18:1+18:2 (89-92%). Therefore MS-2 sunflower oil was found highly adulterated. MS-3 sunflower oil showed the presence of linolenic acid (1.82%) that must be less than 0.6% for pure sunflower oil. Further its palmatic acid (7.97%) and 18:1+18:2 (86.48%) also differed from the ranges for pure sunflower oil (Table 3). Therefore, MS-3 sunflower oil was also found adulterated but its adulteration level was lower as compared to MS-2 sunflower oil. The fatty acid composition of MS-4 sunflower oil (Table 4) showed oleic acid (18:1) to the extent of 62.32%, which resembled to the oleic acid of canola oil. In addition to this the whole fatty acid profile of MS-4 sunflower oil resembled with the fatty acid profile of canola oil. Therefore it is quite clear that MS-4 sunflower oil sample was found containing 100%canola oil instead of sunflower oil. As sunflower oil is expensive than soybean and canola oils in the international market, therefore, it is targeted for adulteration. The fatty acid composition of MS-5, MS-6 and MS-7 canola oil samples (Table 4) resembled with the purity criteria standards as mentioned in Table 3 for canola oil. Therefore, all the canola oil samples were found pure. Similarly fatty acid compositions (Table 4) of MS-8, MS-9 and MS-10 soybean oil samples were found resembling with the purity criteria standards (Table 3) for soybean oil. Therefore, all the three samples of soybean oil were found pure.

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